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Synthesis and Characterization of Dioctyloxybenzo[1,2-*b*:4,3-*b*′]-dithiophene-Containing Copolymers for Polymer Solar Cells

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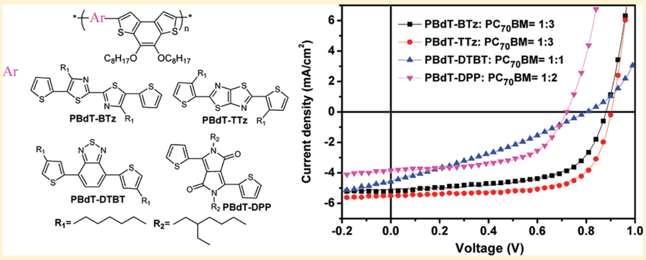
ABSTRACT: A series of D−A copolymers containing dioctyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) donor unit and different acceptor unit of bithiazole (BTz), thiazolo[5,4-*d*]-thiazole (TTz), dithienylylbenzothiadiazole (DTBT), and dithienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP), PBdT-BTz, PBdT-TTz, PBdT-DTBT, and PBdT-DPP, were synthesized for the application as donor materials in polymer solar cells (PSCs). Bandgaps and HOMO (the highest occupied molecular orbital) energy levels of the copolymers were tuned effectively by using different acceptor units from 2.01 and −5.16 eV for PBdT-BTz, to 1.91 and −5.19 eV for PBdT-TTz, 1.70 and −5.09 eV for PBdT-DTBT, and 1.41 and −5.01 eV for PBdT-DPP. The PSCs based on the blend of PBdT-TTz (with a lower HOMO of −5.19 eV) and $PC_{70}BM$ (1:3 w/w) exhibited a power conversion efficiency of 3.40% with a J_{sc} of 5.50 mA/cm^2, a high V_{oc} of 0.90 V, and a high FF of 68.7%.



INTRODUCTION

In the past decade, polymer solar cells (PSCs) have attracted considerable attention as a new potential renewable resource because of their advantages of low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices.[1−3] PSCs are composed of an active layer of the blend of a conjugated polymer donor and a fullerene derivative acceptor, sandwiched between an ITO positive electrode and a low workfunction metal negative electrode. Regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) are the most representative donor and acceptor materials, respectively, and the power conversion efficiency (PCE) of the PSCs based on P3HT/PCBM has reached over 4%.[4] But P3HT has a relatively large band gap (∼2.0 eV) and only harvests photons with wavelength shorter than 650 nm; in addition, its relatively high HOMO (the highest occupied molecular orbital) energy level (−4.76 eV)[5] results in low open-circuit voltage (ca. 0.6 V) of the PSCs with PCBM as acceptor. Therefore, the design and synthesis of new conjugated polymer donor materials with broad absorption and lower HOMO energy level has been one of the most important issues at present.[6] Among many attempts, alternating electron-rich (donor) and electron-deficient (acceptor) copolymerization has been proved to be an effective strategy to tune the band gap and energy levels of polymers.[7−16] To date, the PCE of PSCs based on the donor−acceptor (D−A) copolymers has reached ∼6−7%.[14−16]

Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) has been widely used as donor unit in high performance conjugated D−A copolymer photovoltaic materials for PSCs.[2,14a,16−23] BDT unit possesses a planar structure, and the copolymers containing BDT unit show higher hole mobility. Recently, benzo[2,1-*b*:3,4-*b*′]dithiophene (BDP), which is an isomer of BDT, was also used in photovoltaic copolymer, and the copolymer showed higher photovoltaic performance.[24] Actually, there is another isomer of BDT, benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) (see Scheme 1 for the comparison of the three isomers), which could possess similar property as BDT and BDP. From this consideration, here we synthesized a derivative of benzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) and used it as the donor segment in D−A copolymers. In order to tune the absorption and molecular energy levels to meet the requirements of an ideal donor toward highly efficient photovoltaic performance, we selected several acceptor units to copolymerize with BdT unit, such as 4, 4′-dihexyl-5,5′-di(thiophen-2-yl)-2,2′-bithiazole (BTz), 2,5-bis(3-hexylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole (TTz), 4,7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (DTBT), and 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo-[3,4-*c*]pyrrole-1,4-dione (DPP), and investigated the relationship between their structures and properties.

RESULTS AND DISCUSSION

Synthesis and Thermal Stability. The general synthetic routes for the monomers and copolymers are outlined in Schemes 2 and 3. The alternative D−A copolymers were synthesized by Stille coupling reaction. All the polymers have good solubility in common organic solvents such as chloroform, toluene, and chlorobenzene. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration, and the results are listed in Table 1.

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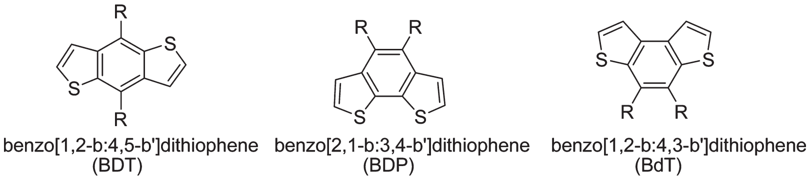
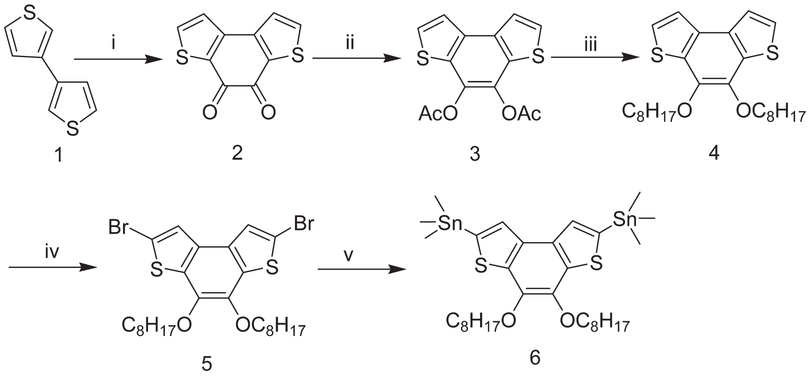
Scheme 1. Molecular Structures of the Isomers of Benzodithiophene



Scheme 2. Synthetic Routes of the Monomers[a]



[a] Reagents and conditions: (i) oxalyl chloride, 1,2-dichloroethane, reflux; (ii) Zn, Ac_2O, CH_2Cl_2; (iii) Cs_2CO_3, $C_8H_{17}I$, CH_3CN; (iv) NBS, $CHCl_3$/HOAC; (v) *n*-BuLi, −78 °C, $(CH_3)_3SnCl$, THF.

Thermal stability of the polymers was investigated with thermogravimetric analysis (TGA), as shown in Figure 1. The TGA analysis reveals that the onset temperatures with 5% weight loss (T_d) of PBdT-BTz, PBdT-TTz, PBdT-DTBT, and PBdT-DPP are 348, 336, 350, and 255 °C, respectively. The slightly lower T_d at 255 °C for PBdT-DPP could be due to the slightly lower stability of DPP unit. Obviously, the thermal stability of the copolymers PBdT-BTz, PBdT-TTz, and PBdT-DTBT is good enough for the applications in optoelectronic devices.

Absorption Spectra. Figure 2 shows the ultraviolet−visible (UV−vis) absorption spectra of the polymer dilute solutions in chloroform and films spin-coated on quartz substrates. For the absorption spectra of the copolymer solutions shown in Figure 2a, PBdT-DTBT and PBdT-DPP exhibited two major absorption bands in the wavelength ranges of 300−500 and 500−900 nm. The peak at longer wavelength could be attributed to the intramolecular charge transfer (ICT) transition, and that at shorter wavelength comes from the $\pi-\pi^*$ transition of the polymer main chain. In contrast, copolymers PBdT-BTz and PBdT-TTz have one absorption band in the range of 300−650 nm which is in coincidence with the weak electron-deficient ability of bithiazole and thiazolothiazole units. Apparently, PBdT-DPP has a much extended absorption with the absorption maximum at 650 nm, in agreement with the strong electron-deficient ability of DPP unit. The absorption spectra of the four polymers in thin films are shown in Figure 2b, and the optical properties are summarized in Table 2. The shape of the peaks and the trend of the absorption wavelength were generally similar to those of the polymer solutions. The absorption maxima of the polymer films all red-shifted in comparison with that in solutions, which is a common phenomenon for the conjugated polymers owing to the aggregation of the conjugated polymer main chains in the solid films. In addition, PBdT-DPP exhibited a broad peak from 650 to 710 nm, indicating that there is a strong interchain interactions and good $\pi-\pi$ stacking in solid-state polymer films.

HOMO and LUMO Energy Levels. The electrochemical cyclic voltammetry was performed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers.[25] Figure 3 shows the cyclic voltammograms (CVs) of the copolymer films on Pt disk electrode in 0.1 mol/L Bu_4NPF_6 acetonitrile solution. The onset reduction potentials (φ_{red}) of PBdT-BTz, PBdT-TTz, PBdT-DTBT and PBdT-DPP are −1.89, −1.81,-1.61 and −1.35 V vs. Ag/Ag$^+$, respectively, while the onset oxidation potentials (φ_{ox}) are 0.45, 0.48, 0.38, 0.33 V vs Ag/Ag$^+$, respectively. From φ_{ox} and φ_{red} of the polymers, HOMO and LUMO energy levels as well as the energy bandgap (E_g^{EC}) of the polymers were calculated according to the equations[5,26]

$$\text{HOMO} = -e(\varphi_{ox} + 4.71)\ (\text{eV});$$
$$\text{LUMO} = -e(\varphi_{red} + 4.71)\ (\text{eV});$$
$$E_g^{EC} = e(\varphi_{ox} - \varphi_{red})\ (\text{eV})$$

where the units of φ_{ox} and φ_{red} are V vs Ag/Ag$^+$. The results of the electrochemical measurements are listed in Table 2. All the copolymers exhibit relatively deep HOMO energy levels (<−5.0 eV) which will lead to higher open-circuit voltage (V_{oc}) of the PSCs based on these copolymers as donor, since V_{oc} of the PSCs is proportional to the difference between the LUMO of the electron acceptor and the HOMO of the electron donor.[27]

Hole Mobility. Hole mobility is another important parameter for the conjugated polymer donor photovoltaic materials. Here we measured the hole mobilities of the copolymers by space-charge limit current (SCLC) method by using a device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices,

Scheme 3. Synthetic Routes of the Copolymers

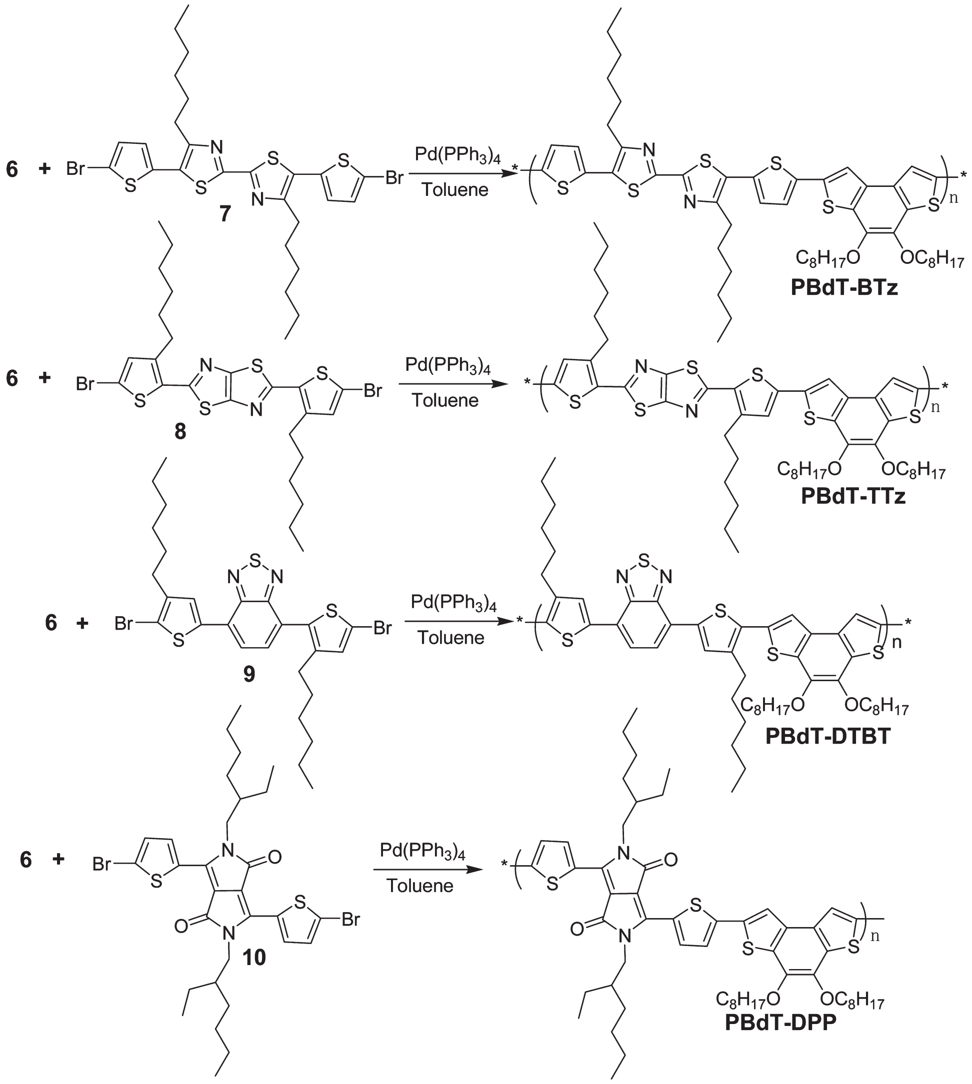


Table 1. Molecular Weights and Thermal Properties of the Polymers

polymers	M_w[a]	M_n[a]	PDI[a]	T_d (°C)[b]
PBdT-BTz	31.3K	20.2K	1.55	348
PBdT-TTz	17.2K	11.3K	1.52	336
PBdT-DTBT	19.1K	11.2K	1.70	350
PBdT-DPP	14.3K	9.1K	1.57	255

[a] M_n, M_w, and PDI of the polymers were determined by GPC using polystyrene standards in THF. [b] The 5% weight loss temperatures under an inert atmosphere.

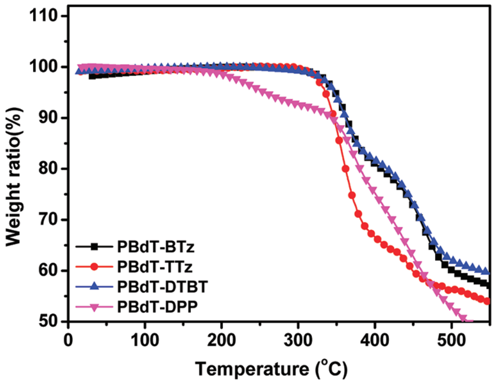


Figure 1. TGA plots of the copolymers with a heating rate of 10 °C/min under an inert atmosphere.

SCLC is described by[28]

$$J \cong (9/8)\varepsilon\varepsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/E_0 L})/L^3 \qquad (1)$$

where ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, L is the thickness of the films, and $V = V_{appl} - V_{bi}$; V_{appl} is the applied potential, and V_{bi} is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{bi} = 0.2$ V). Figure 4 shows the $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$

plots of the polymers measured based on the SCLC method. According to eq 1, the hole mobilities obtained from the data in Figure 4 are 5.53×10^{-4}, 1.81×10^{-3}, 1.67×10^{-5}, and 1.66×10^{-3} $cm^2/(V\ s)$ for PBdT-BTz, PBdT-TTz, PBdT-DTBT, and PBdT-DPP, respectively. Obviously, the hole mobilities of the polymers except for PBdT-DTBT are good for the application as photovoltaic donor materials in PSCs.

Photovoltaic Properties. To investigate and compare the photovoltaic properties of the four copolymers, bulk heterojunction PSC devices with a configuration of ITO/PEDOT:PSS/polymers:$PC_{70}BM$/Ca/Al were fabricated. Figure 5 shows the $J-V$ curves of the PSCs under the illumination of AM1.5, 100 mW/cm^2, and the photovoltaic parameters of the PSCs are summarized and listed in Table 3. The PSCs based on PBdT-BTz, PBdT-TTz, or PBdT-DTBT all exhibited high open-circuit voltage (V_{oc}) over 0.8 V, benefitted from the deep HOMO energy levels of the polymers.[29] In contrast, the device based on PBdT-DPP demonstrated a low V_{oc} of 0.71 V, which is consistent with its relatively higher HOMO level. The PSCs based on PBdT-DTBT exihibited lower FF of 30.7% which could be caused by its lower hole mobility. The power conversion efficiency (PCE) of the PSC based on PBdT-BTz/$PC_{70}BM$ (1:3 w/w) reached 2.81% with a short-circuit current (J_{sc}) of 5.20 mA/cm^2, a higher open-circuit voltage (V_{oc}) of 0.88 V, and a FF of 61.3%. The PSC based on PBdT-TTz/$PC_{70}BM$ (1:3 w/w) exhibited an even higher PCE of 3.40% with a J_{sc} of 5.50 mA/cm^2, a V_{oc} of 0.90 V, and a high FF of 68.7%. The high FF of the device based on PBdT-TTz/$PC_{70}BM$ could be benefited from the higher hole mobility of PBdT-TTz. But the FF (56.1%) of the PSC based on PBdT-DPP/$PC_{70}BM$ is lower than that (61.3%) of the device based on PBdT-BTz/$PC_{70}BM$ although the hole mobility (1.66×10^{-3} $cm^2/(V\ s)$) of PBdT-DPP is higher than that (5.53×10^{-4} $cm^2/(V\ s)$) of PBdT-BTz. Probably, the lower photocurrent influenced the fill factor of the device based on PBdT-DPP/$PC_{70}BM$.

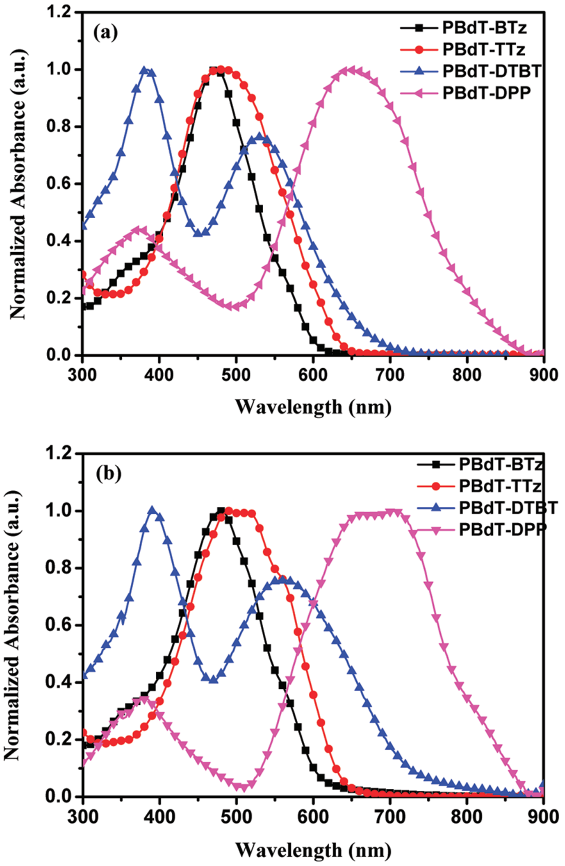


Figure 2. Absorption spetra of the copolymers: (a) in chloroform solutions; (b) in solid films.

It should be mentioned that the weight ratios of the polymer/$PC_{70}BM$ are different for different polymers in the comparison of their photovoltaic properties. Actually, we performed optimization of the photovoltaic performance of the PSCs by changing the weight ratios for each polymer, and we compared the photovoltaic properties of the polymers with the optimized weight ratios in Figure 5 and Table 3.

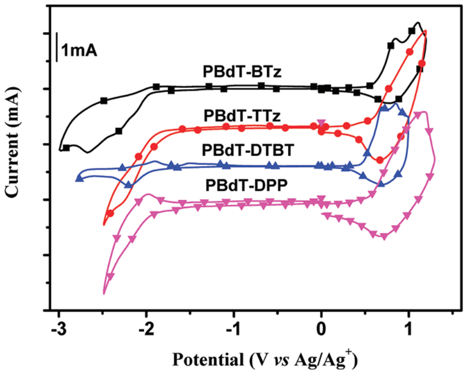


Figure 3. Cyclic voltammograms of copolymers film on a platinum plate electrode measured in 0.1 mol/L Bu_4NPF_6 acetonitrile solutions at a scan rate of 100 mV/s.

Table 2. Optical and Electrochemical Properties of the Polymers

	UV–vis absorption spectra				cyclic voltammetry		
	solution	film			p-doping	n-doping	
polymers	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	φ_{ox}/HOMO (V)/(eV)	φ_{red}/LUMO (V)/(eV)	E_g^{EC} (eV)
PBdT-BTz	475	481	615	2.01	0.45/−5.16	−1.89/−2.82	2.34
PBdT-TTz	485	520	650	1.91	0.48/−5.19	−1.81/−2.90	2.29
PBdT-DTBT	532	560	733	1.70	0.38/−5.09	−1.61/−3.10	1.99
PBdT-DPP	650	710	880	1.41	0.33/−5.01	−1.35/−3.36	1.68

Figure 6 shows the external quantum efficiency (EQE) curve of the PSC based on PBdT-TTz:$PC_{70}BM$. It can be seen that the EQE curve covers a broad wavelength range from 300 to 700 nm with the maximum EQE value of 43% at ca. 475 nm. The integral

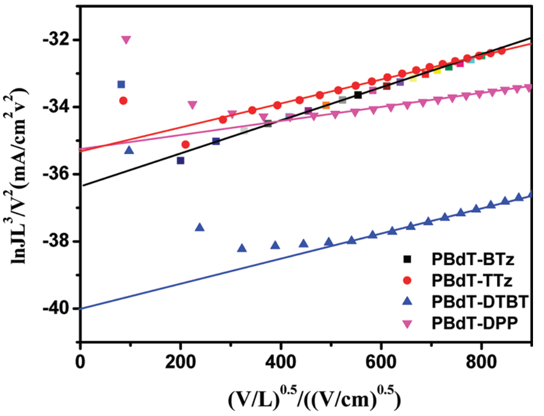


Figure 4. Plot of $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ of the polymers for the measurement of hole mobility by the SCLC method.

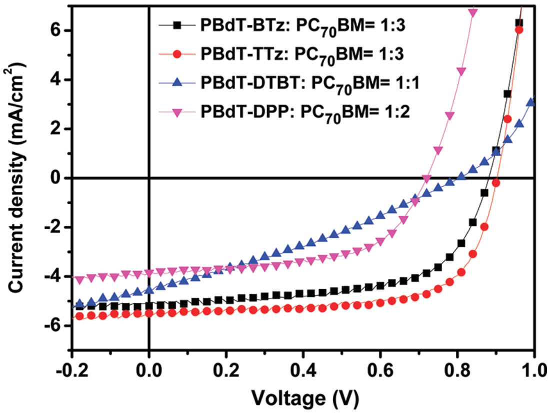


Figure 5. $J-V$ curves of the PSCs based on polymers: $PC_{70}BM$ under the illumination of AM 1.5, 100 mW/cm^2.

Table 3. Photovoltaic Performances of the PSCs Based on Polymer:$PC_{70}BM$ under the Illumination of AM1.5, 100 mW/cm^2

polymers	blend ratio with $PC_{70}BM$	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PBdT-BTz	1:3	0.88	5.20	61.3	2.81
PBdT-TTz	1:3	0.90	5.50	68.7	3.40
PBdT-DTBT	1:1	0.80	4.58	30.7	1.13
PBdT-DPP	1:2	0.71	3.28	56.1	1.31

of the EQE is in good agreement with the J_{sc} value measured from the $J-V$ curve.

The photovoltaic properties of the D−A copolymers reveal that TTz is a good acceptor unit to copolymerize with BdT donor unit, and the PSC based on PBdT-TTz:$PC_{70}BM$ demonstrated high V_{oc} of 0.90 V and a high FF of 68.7%. Interestingly, in comparison with PBdT-TTz, the copolymer of TTz with BDT showed lower V_{oc} of 0.76−0.77 V and a lower FF of 51−56.7%,[30] indicating that BdT is a supervior donor unit than BDT when copolymerizing with TTz acceptor unit for the application as polymer donor materials in PSCs.

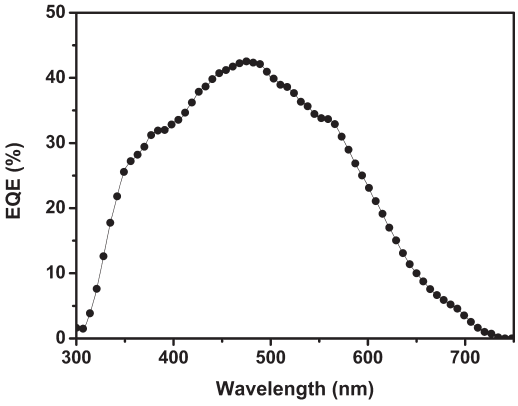


Figure 6. EQE of PSC based on PBdT-TTz: $PC_{70}BM$ (1:3, w/w).

■ CONCLUSION

We have sythesized a series of copolymers containing dioctyloxybenzo[1,2-*b*:4,3-*b*′]dithiophene (BdT) units, PBdT-BTz, PBdT-TTz, PBdT-DTBT, and PBdT-DPP, by the Pd-catalyzed Stille-coupling method. Band gaps of the copolymers were modulated from 2.01 to 1.41 eV, and their HOMO energy levels were tuned from −5.01 to −5.19 eV by using different acceptor units. The PSCs based on the blend of PBdT-TTz (with HOMO level of −5.19 eV) and $PC_{70}BM$ (1:3 w/w) exhibited a PCE of 3.40% with a J_{sc} of 5.50 mA/cm^2, a high V_{oc} of 0.90 V, and a higher FF of 68.7%. The results indicate that the BdT unit could be also a good donor unit in composing the D−A copolymers for the application in high performance PSCs.

■ EXPERIMENTAL SECTION

Materials. All chemicals and solvents were reagent grades and purchased from Aldrich, Alfa Aesar, and TCI Chemical Co. Toluene, tetrahydrofuran, and diethyl ether were distilled to keep anhydrous before use. All of the other chemicals were used as received.

Measurements and Characterization. All new compounds were characterized by ^1H NMR spectroscopy performed on a Bruker DMX-400 spectrometer. For the ^1H NMR measurements, $CDCl_3$ was used as the solvent. Chemical shifts in the NMR spectra were reported in ppm relative to the singlet at 7.26 ppm for $CDCl_3$. The molecular weight of the polymers was measured by gel permeation chromatography (GPC), and polystyrene was used as a standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV−vis absorption spectra were obtained on a Hitachi U-3010 spectrometer. Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu_4NPF_6 in acetonitrile at a scan rate of 100 mV/s. The polymer films were coated on a Pt plate electrode (1.0 cm^2) by dipping the electrode into the corresponding solutions and then drying. A Pt wire was used as the counter electrode, and Ag/Ag$^+$ was used as the reference electrode.

Device Fabrication and Characterization of Polymer Solar Cells. Polymer solar cells (PSCs) were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode, and the blend film of the polymer/$PC_{70}BM$ between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and $PC_{70}BM$ in *o*-dichlorobenzene on the ITO/PEDOT:PSS electrode. Then the Ca/Al cathode was deposited on the polymer layer by vacuum evaporation under 5 × 10^{-5} Pa. The thickness of the photosensitive layer is ca. 100 nm measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is 4 mm^2. The current−voltage ($I-V$) measurement of the devices was conducted on a computer-controlled Keithley 236 source measure unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm^2.

Synthesis. The synthetic routes of the monomer and polymers are shown in Schemes 2 and 3. The compounds **7**,[31] **8**,[32] **9**,[33] and **10**[34] were synthesized according to the procedure in the literature. The detailed synthetic processes are as follows.

*Benzo[1,2-b:4,3-b′]dithiophene-7,8-quinone (**2**)*[35]. Oxalyl chloride (6.0 mL, 69 mmol) was added to a flask containing 3,3′-bithienyl (20.0 g, 120 mmol) dissolved in 1,2-dichloroethane (350 mL), and the mixture, under a $CaCl_2$ drying tube open to the atmosphere, was refluxed for 5 days. More oxalyl chloride (6.0 mL, 69 mmol) was added, and reflux was continued for another 5 days; after that, the mixture was cooled to 25 °C and left to stand overnight. Then the reaction mixture was filtered, and the filter cake was triturated thoroughly with hexanes and warm ethanol. Red solid **2** (18 g) was obtained. Yield: 68%. GC-MS: m/z = 220. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.82 (d, 2H), 7.29 (d, 2H).

*7,8-Diacetoxybenzo[1,2-b:4,3-b′]dithiophene (**3**)*[35]. Dry CH_2Cl_2 (300 mL) was added by cannula to a flask containing **2** (5.6 g, 25 mmol) and Zn dust (16.6 g, 250 mmol). Acetic anhydride (24 mL, 250 mmol) and triethylamine (53 mL, 380 mmol) were sequentially syringed in. The mixture was stirred for 4 h at 25 °C and then filtered through Celite. The filtrate was washed with water, 1 M HCl, saturated aqueous $NaHCO_3$, and again with water. The organic layer was dried (Na_2SO_4), filtered, treated with activated charcoal, and filtered again through Celite. Removal of solvent under reduced pressure and further drying under high vacuum yielded 6.34 g of **3**, an off-white solid. Yield: 83%. GC-MS: m/z = 306. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.62 (d, 2H), 7.51 (d, 2H), 2.41 (s, 6H). Yield: 68%

*7,8-Dioctyloxybenzo[1,2-b:4,3-b′]dithiophene (**4**)*[35]. A flask containing **3** (6.34 g, 20.7 mmol) and Cs_2CO_3 (16 g, 103 mmol) was fitted with a reflux condenser. Acetonitrile (300 mL) was added through a cannula, and 1-iodoocane (33 mL, 103 mmol) was syringed in. The mixture was stirred and refluxed for 3 days; after that, it was cooled to 25 °C. The solvent was removed under reduced pressure, and the remaining solids were partitioned between CH_2Cl_2 and water. The organic layer was washed with 1 M HCl and with water, dried (Na_2SO_4), and filtered. The solvent was removed, and the product was triturated thoroughly with cold ethanol and dried under high vacuum, yielding 8.3 g of **5**, off-white, waxy solid. Yield: 90%. GC-MS: m/z = 446. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.62 (d, 2H), 7.45 (d, 2H), 4.22 (t, 4H), 1.84 (quint, 4H), 1.54 (quint, 4H), 1.20−1.40 (m, 16H), 0.87 (m, 6H).

*2,5-Dibromo-7,8-diacetoxybenzo[1,2-b:4,3-b′]dithiophene (**5**)*. Compound **4** (4.46 g, 10.00 mmol) was dissolved in a mixture of chloroform (100 mL) and acetic acid (100 mL). NBS (3.56 g, 20 mmol) was then added to the solution, which was then stirred for 10 h in the dark. The product was poured into water (200 mL); the solution was extracted with chloroform (100 mL × 3) and dried by magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, petroleum) to afford **5** (5.2 g), an off-white solid. Yield: 86%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.49 (s, 2H), 4.25 (t, 4H), 1.87−1.26 (m, 24H), 0.87 (m, 6H).

*2,5-Bis(trimethyltin)-7,8-diacetoxybenzo[1,2-b:4,3-b′]dithiophene (**6**)*. Compound **5** (3.02 g, 5 mmol) and 100 mL of THF were added into a flask under an inert atmosphere. The solution was cooled down to −78 °C by a liquid nitrogen−acetone bath, and 4.4 mL of *n*-butyllithium (11 mmol, 2.5 M in *n*-hexane) was added dropwise. After being stirred at −78 °C for 1 h, a great deal of white solid precipitate appeared in the flask. Then, 15 mmol of trimethyltin chloride (15 mL, 1 M in *n*-hexane) was added in one portion, and the reactant turned to clear rapidly. The cooling bath was removed, and the reactant was stirred at ambient temperature for 2 h. Then, it was poured into 200 mL of cool water and extracted by ether three times. The organic layer was washed by water two times and then dried by anhydrous $MgSO_4$. After removing solvent under vacuum, the residue was used in next step for the copolymerization without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.72 (s, 2H), 4.25 (t, 4H), 1.87−1.26 (m, 24H), 0.87 (m, 6H), 0.52(s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 141.9, 139.0, 138.2, 132.4, 130.2, 77.6, 77.2, 76.9, 73.7, 32.1, 30.7, 29.7, 29.6, 26.4, 22.9, 14.4, −8.0.

General Procedure for the Synthesis of Copolymers. These four polymers were synthesized with the same procedure of coupling dibromide compounds with bis(trialkylstannyl)-substituted compounds. 0.5 mmol of dibromide compound, 0.5 mmol of bis(trialkylstannyl)-substituted compound, and dry toluene (12 mL) were added to a 50 mL double-neck round-bottom flask. The reaction container was purged with argon for 20 min to remove O_2, and then Pd $(PPh_3)_4$ (15 mg) was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 14 h. The reactant was cooled down to room temperature, poured into MeOH (200 mL), and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The polymer was purified by chromatography on silica gel with chloroform as the eluent, and the polymer solution was concentrated and was poured into MeOH. Then the precipitates were collected and dried under vacuum overnight.

PBdT-BTz. 225 mg. Yield: 47%. GPC: M_w = 31.3K; M_n = 20.2K; M_w/M_n = 1.51. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.75−7.55 (br, 6H), 4.25 (br, 4H), 2.85 (br, 4H), 1.82−0.87 (m, 52H). Anal. Calcd for $C_{53}H_{69}N_2O_2S_6$ (%): C, 66.41; H, 7.26; N, 2.92. Found (%): C, 65.32; H, 7.15; N, 2.73.

PBdT-TTz. 192 mg. Yield: 42%. GPC: M_w = 17.2K; M_n = 11.3 K; M_w/M_n = 1.52. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.71−6.85 (br, 4H), 4.25 (br, 4H), 2.95 (br, 4H), 1.84−0.87 (m, 52H). Anal. Calcd for $C_{50}H_{64}N_2O_2S_6$ (%): C, 65.46; H, 7.03; N, 3.05. Found (%): C, 65.37; H, 6.89; N, 2.88.

PBdT-DTBT. 204 mg. Yield: 45%. GPC: M_w = 19.1K; M_n = 11.2K; M_w/M_n = 1.70. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.20−6.95 (m, 6H), 4.25 (br, 4H), 2.63 (m, 4H), 1.81−0.90 (m, 52H). Anal. Calcd for $C_{52}H_{66}N_2O_2S_5$ (%): C, 68.53; H, 7.30; N, 3.07. Found (%): C, 67.32; H, 7.15; N, 2.97.

PBdT-DPP. 250 mg. Yield: 50%. GPC: M_w = 14.3K; M_n = 9.1K; M_w/M_n = 1.57. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.72−6.99 (br, 6H), 4.25 (br, 4H), 3.01 (br, 4H), 2.01−0.87 (m, 60H). Anal. Calcd for $C_{57}H_{77}N_2O_4S_4$ (%): C, 69.68; H, 7.90; N, 2.85. Found (%): C, 68.56; H, 7.69; N, 2.68.

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